The Roles of Hydrazine and Ethylenediamine in Wet Synthesis of Cu Nanowire

Harsojo[1,*], Lutfi Ayu Puspita[2], Dedi Mardiansyah[1,3], Roto Roto[2], and Kuwat Triyana[1]

[1]*Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia*

[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia*

[3]*Department of Physics Education, Faculty of Teaching and Education, Pasir Pengaraian University, Riau, Indonesia*

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ABSTRACT

A wet synthesis Cu nanowire using $CuNO_3$ as a precursor and hydrazine as a reduction agent and ethylene diamine as a polymer capping agent in excessive sodium hydroxide solution 15 M NaOH has been done. The study was done by varying the volume of hydrazine 0.15, 0.25 and 0.75 mL and ethylenediamine (EDA) (0.5, 1.5 and 0.25 mL) in a total volume of 100 mL, to investigate the roles of these two agents in forming the nanowire and was done at 60 °C at 60 RPM stirring speed. The study revealed that the wet synthesis could be used to produce nanowires in the length of micrometers with a diameter of about hundred nanometers. The best CuNW was obtained at volume EDA 1.5 mL at hydrazine volume 0.15 mL with length to diameter ratio was 120 ± 30*. The roles of both hydrazine and the EDA in the process of making nanowires and nanoparticles were also discussed.*

Keywords: *Cu nanowire; hydrazine; wet synthesis; EDA*

ABSTRAK

Telah dilakukan sintesis basah untuk membuat kawat nano Cu dengan menggunakan $(CuNO_3)_2$ $3H_2O$ sebagai materi prekursor, hidrasin sebagai reduktor oksigen, dan ethylenediamine sebagai bahan polimer pembentuk dan pelapis kawat. Sintesis dilakukan dalam suasana basa natrium berlebih, 15 M dengan pH = 12 dan suhu 60 °C dengan putaran adukan 60 RPM. Kajian dilakukan dengan melakukan variasi volume hidrasin (0,15, 0,25 dan 0,75 mL) dan ethylenediamine (EDA) (0,5, 0,15, dan 0,25 mL) pada volume 100 mL dan peran kedua bahan dalam menghasilkan kawat nano tembaga. Hasil kajian menunjukkan bahwa dengan sintesis basah ini dapat dihasilkan kawat nano tembaga dalam kisaran panjang mikrometer dan diameter sekitar seratus nanometer. Hasil optimum kawat nano tembaga berukuran sekitar seratus nanometer dengan panjang mikrometer diperoleh pada volume hidrazin 0,15 mL dan volume EDA 1,5 mL dengan perbandingan panjang terhadap diameter 120 ± 30*. Dilakukan pula pembahasan tentang peran hidrazin dan EDA di dalam membentuk nanopartikel dan nanowire.*

Kata Kunci: *kawat nano Cu; hidrazin; sintesis basah; EDA*

INTRODUCTION

Metal nanowires have drawn attention many researchers for a decade since such wires have a potential to be used in many applications such as transparent electrodes, different kind of sensors, as well as electrodes in batteries and supercapacitors. However, the needs of such requirements still require further exploration, especially regarding the synthesis optimization, scaling up, and producing a cheaper synthesis for scaled up production. Although the synthesis of the silver nanowire to meet the requirement of the transparent electrode has almost been established, but the use of copper nanowire is more demanded since besides its electrical and optical performance to be comparable to silver, moreover, it has more benefit because it has a cheaper price and a higher abundance in nature. Therefore, the search for the synthesis of copper nanowire was still attracted much attention.

Many authors have studied different kinds methods to synthesize copper nanowires, including synthesis using template materials [1-6], solvothermal or hydrothermal [7,8], and wet synthesis [9-13]. Although the template technique produces a quite clean and straight copper nanowires, but the process requires cleaning the sacrificed materials which considered as a delicate and time-consuming process. The solvothermal and template technique might produce a long nanowire ranging about hundred

* Corresponding author. Tel : +62-8156887664
Email address : harsojougm@ugm.ac.id

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nanometers in diameter with ten micrometers in length [1-8], but the process usually took a number of hours. And therefore, it is considered as time-consuming. However, these are still used as powerful techniques to synthesize nanowire in the high crystalline ratio. The wet synthesis in producing copper nanowires had been explored by many authors using different capping agents and reductors [8-13]. Perhaps, the simplest and fastest in producing copper nanowire in wet synthesis is done using copper salt, N_2H_4 (hydrazine) as a reductor, and an amine group as a capping agent such as done by Rathmell and his group [11-12]. They produced a successful wet synthesis in preparing the Cu nanowire using $CuNO_3$ as a precursor, hydrazine as a reductor, and ethylenediamine (EDA) as a capping agent in about 30 min. The used of hexadecylamine as the capping and stabilizing agent and glucose in synthesizing ultralong CuNWs was done in Ref. 13. However, this process might still be considered as a long time one. A further study was carried by another group using hydrazine as the reductor but by replacing ethylenediamine with oleylamine solution through a $Ni(acac)_2$ catalytic formation process in searching the effective process [14]. Using ethylenediamine tetraacetic acid (EDTA) as capping agent and Na OH together with supercritical water, the synthesis of CuNW was carried successfully from a precursor copper sulfate [8].

In producing nanowires for the transparent electrode application a good conductivity and optical transparency were the key parameters. Assuming stability of the wires can be handled, these key factors relied upon the diameter and the length of the wire. In short, it is fairly accepted that the quality of the nanowires functioned as a transparent electrode depending upon their length to diameter ratios [11,12]. The result of Rathmell [11] in producing Cu nanowire at quite low temperature in a very short time was quite promising. However, it was still not clear how to control the dimension of the wire using a different concentration or volume of EDA. The study of EDA as capping agent was done in Ref. [11]. However, the role of both EDA and hydrazine was still required further investigation. Therefore, an information related to control the dimension of the wire using EDA and hydrazine was still considered as an important issue. This study was done in the trial to provide such information in synthesizing of the targeted Cu nanowire.

EXPERIMENTAL SECTION

Materials

The experiment was done using $Cu(NO_3)_2\ 3H_2O$ (99%-104%, Sigma-Aldrich) prepared in 20 mL (0.025 M), NaOH (>98%, Sigma-Aldrich) prepared in 100 mL (15 M) in deionized water, ethylenediamine or EDA (>99.5%, Sigma-Aldrich) (60 M), N_4H_2 (hydrate 80% Sigma-Aldrich) (1.09 M) volume was varied from 0.25 to 0.75 mL. The total volume of the solution was managed to be 100 mL. The use of high molar NaOH was selected since this was expected to decrease the size of the nanoparticle Cu as done in Ref. 12.

Instrumentation

Several instruments were used to characterize the result. The microstructure characterization of the was carried out using Scanning Electron Microscope (JEOL 560 XL) operated at 10 kV, and Transmission Electron Microscope (JEM 1400) operated at 100 kV. The X-ray diffraction was done using Phillip PW 3710 operating at 20 kV using a copper anode. The UV-Vis absorption spectra were taken using Shimadzu UV-1800 spectrometer.

Procedure

The synthesis process was done according to the method described in Ref. [11] with a little modification. In this reaction, we reduced down to about a hundredth smaller with a lower temperature, with a slower stirring speed. In a typical copper nanowire synthesis, we used 60 g of NaOH in aquadest 100 mL, mixed with 0.12 g $Cu(NO_3)_2\ 3H_2O$ in 20 mL aquadest. The solution was kept at 60 °C, stirred at about 60 RPM for about half an hour to reach homogeneous condition indicated by a deep clear blue color. The following reaction took place in this process, $Cu(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + 2NaNO_3(aq)$ and $N_2H_4+2Cu(OH)_2 \rightarrow 2NO_2+4H_2+4Cu$. The second process changes the Cu ion into Cu atom through reduction. In the addition of EDA, Cu ion can be chelated by EDA. Three molecules of EDA can chelate one ion Cu^{2+}. The addition of hydrazine will reduce these ions to become neutral atoms.

The each EDA volume of 0.5, 1.0, and 1.5 mL was then mixed in the solution keeping a steady temperature of 60 °C for 2 min under similar stirring condition. Prior being used, we diluted the N_2H_4 (80%) using deionized water into N_2H_4 (35%). Eventually, each of the N_2H_4 volumes of 0.15, 0.25, and 0.75 mL was added to the solution. The color of the solution changed slowly from deep clear blue into milky white and then into dark red, indicating the formation of thin Cu NWs. By letting this condition in about 30 min, the solution showed a segregation of Cu NWs floating on top of the solution surface. The floating of Cu NWs was then separated from the solution and centrifuged at 10000 RPM for about an hour. The supernatant was then rinsed and centrifuged five times using alcohol to

get a clear Cu NW in an alcohol solution. We added hydrazine (35%) 0.001 mL in 25 mL CuNW in an alcohol solution to prevent the oxidation. This final solution was kept at -4 °C in a closed bottle for further usage. Instead of using the concentration or molar value, in our experiment we used hydrazine and EDA expressed in volume unit for a practical reason. For scaled up production, the calculation using molar value should be done accordingly.

RESULT AND DISCUSSION

The CuNW which were extracted from the synthesis and prepared in the alcohol solution was checked by UV-Vis spectrometer. The result was shown in Fig. 1. The peaks of the absorption spectra for the synthesis using EDA 0.5, 1.0, and 1.5 mL while the volume of hydrazine fixed in 0.15 mL appeared at 620, 625, and 626 nm, respectively (Fig. 1). The result indicated that these different volumes of the EDA produced only a little effect in plasmon peaks of the final product of CuNW in the alcohol solution. Although, these different peak positions and their widths usually are related to the size and diameter of the Cu wires, from the peaks we can only recognize clearly that these peaks are related to the existence of the CuNW in the solution. The effect of EDA volume (0.5, 1.0, and 1.5 mL) used in the synthesis to the nanowire sizes was more clearly seen using SEM, presented at Fig. 2. From this micrography, we can see that when no EDA used in the solution, only Cu nanoparticles (CuNPs) formed with the average size of about 100 nm as shown in Fig. 2(a). In addition, the CuNPs are agglomerated due to their reactivity. When EDA (0.5, 1.0, and 1.5 mL) used in the synthesis, the synthesis produces CuNW having different length and diameter. We found that the best size of a length over diameter ratio was obtained at EDA 1.5 mL as shown in Fig. 2(c). We notice that a greater volume EDA produced CuNW accompanied by more CuNPs. This means that there is an optimized condition in which the amount of EDA helping to transform the CuNP into CuNW. Therefore EDA is called as a capping agent or a guiding agent.

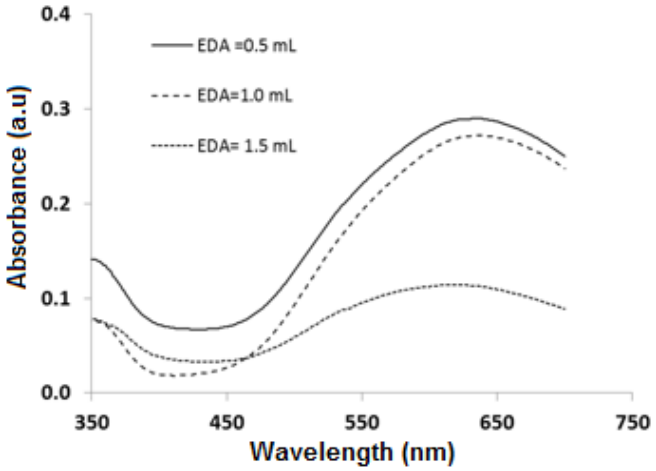

Fig 1. Absorbance spectra of Cu NW synthesized by a different EDA volume at 0.1 mL of hydrazine

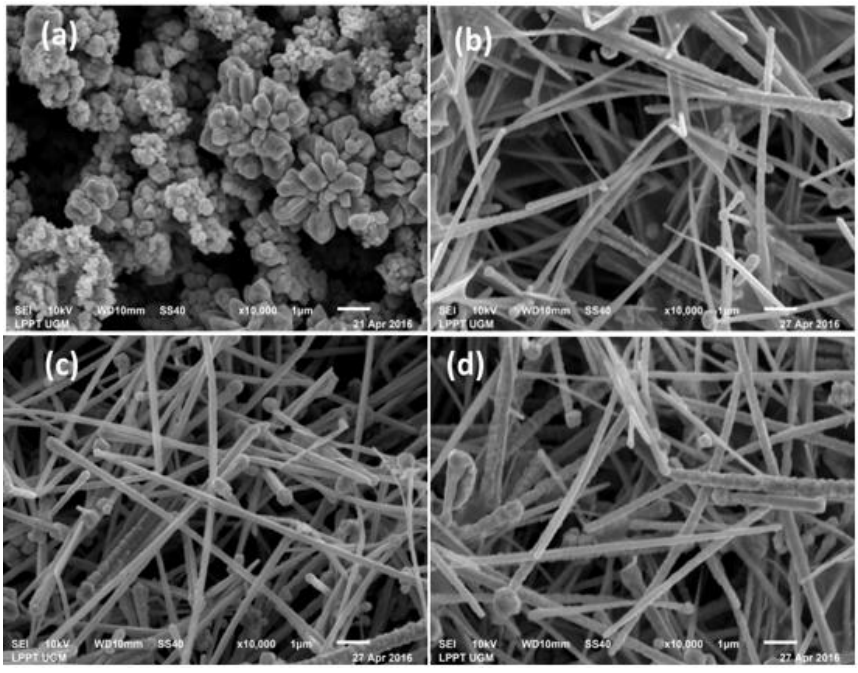

Fig 2. The result of wet synthesis using EDA volume (a) 0 mL (b) 0.5 mL (c) 1.0 mL(d) 1.5 mL at 0.1 mL hydrazine. All result was done at about 60 °C, stirred at 70 rpm

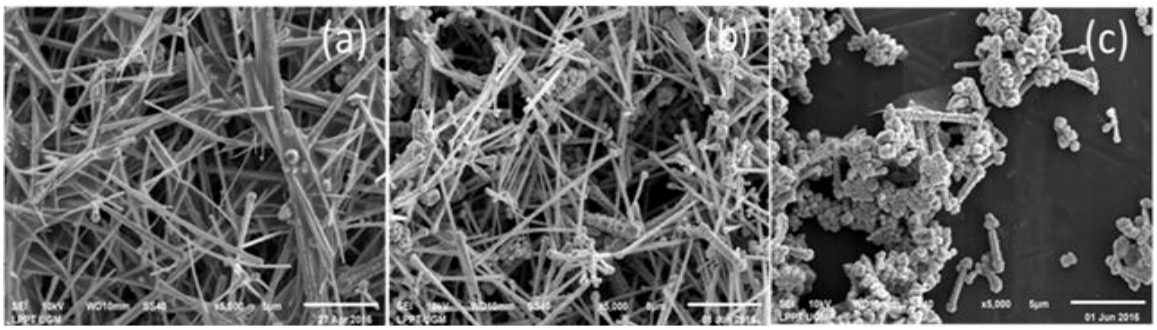

Fig 3. The effect of hydrazine volume (a) at volume of 0.15 mL (b) 0.25 mL (c) 0.35 mL at EDA 1.5 mL

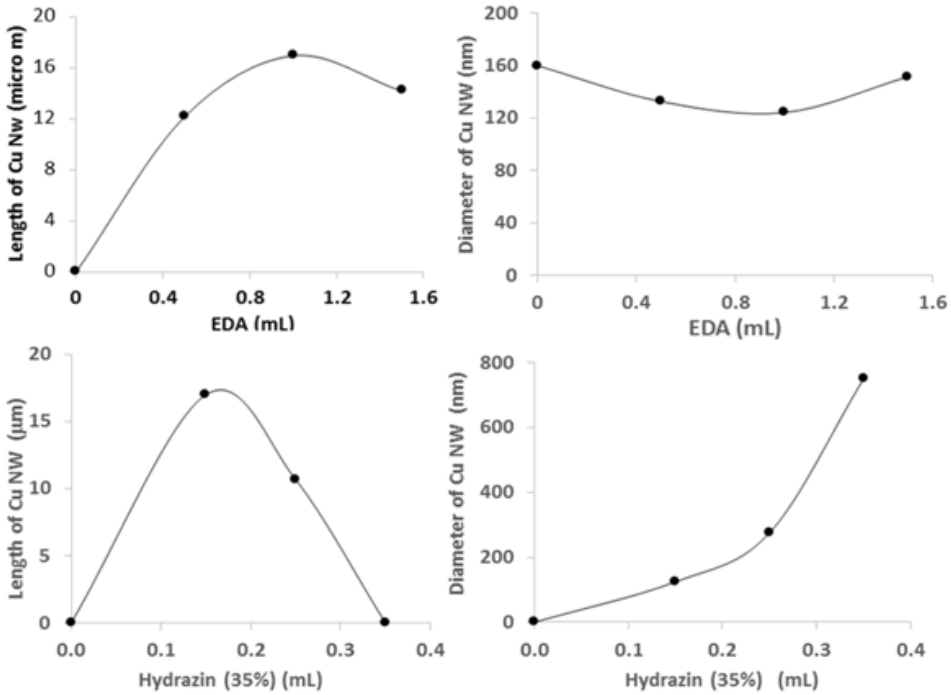

Fig 4. The size of CuNW versus the volume of hydrazine and EDA indicating the hydrazine at a volume of 0.15 mL and the EDA 1.5 mL producing the best CuNW in term of the length over the diameter ratio

We hypothesize the following mechanism. As in our synthesis, we use the strong base of Na OH (pH = 12) at the fixed amount of $CuNO_3$, the sizes of the CuNWs were controlled either by hydrazine and EDA. This was understood since the role of hydrazine acted as a strong reduction agent from Cu^{++} into Cu atom. Without EDA the following reaction takes place. First, the royal blue color of the solution indicates the existence of 4[Cu(OH)]. When the hydrazine is added, the following reaction occur $4[Cu(OH)]^{2+} + N_2H_4$ (aq)→$2Cu_2O(s) + N_2(g)+6H_2O+8OH^-$ followed by the reaction $2CuO(s)+N_2H_4(aq)→4Cu(s)+ N_2(g)+ 2H_2O$. Therefore, only Cu and Cu_2O nanoparticles produced. This was supported by Fig. 2(a). However, when the EDA used is 0.5 mL up to 1.5 mL in the solution, it can suppress Cu_2O, and the synthesis allows the growing of CuNP into CuNW. The stirring and the heating condition helped this growth. This result is supported by Fig. 2(b) to Fig. 2(d). Therefore, it can be understood that at a constant volume of hydrazine, this synthesis depends on the volume of EDA used. We found that the diameters of wires were in the range of 90 nm up to 200 nm.

Meanwhile, the existence of hydrazine in the reaction mainly functions to reduce Cu^{++} into Cu atom with finally becoming CuNPs [11-12]. Therefore, without EDA, as a capping agent, only the agglomeration of CuNPs were produced When EDA fixed 1.5 mL, and the hydrazine volume of 0.15, 0.25, and 0.75 mL used in the synthesis, we get a mixture of CNPs and CuNWs as presented in Fig. 3. Using hydrazine 0.15 mL, maximum CuNWs were produced while at hydrazine volume of 0.25 mL, the synthesis produced shorter wires accompanied by more CuNP

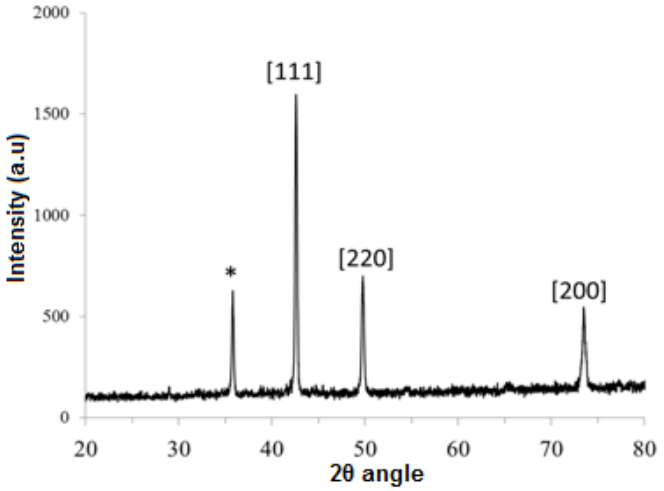

Fig 5. X-ray diffraction of powder Cu nanowire with the planes indicating Cu peaks. The symbol * indicates for [111] Cu_2O plane

compared to that of 0.15 mL. This means that using hydrazine volume of 0.25 mL, the synthesis starts producing an unbalancing the process of transforming CuNP into CuNW using the available EDA. The result was shown in Fig. 3(b). In addition, at hydrazine volume of 0.75 mL, creating the bigger unbalancing process in transforming CuNP into CuNW, therefore more CuNPs and short CuNWs were produced as shown in Fig. 3(c).

The result also told that the amount of hydrazine volume used in the synthesis produced a more sensitive effect to the size of CuNW compared to the amount of EDA volume added to the solution as can be seen in Fig. 3 and Fig. 4. This suggested that as hydrazine was not only the main agent transforming Cu^{++} into Cu atoms but also the critical agent in transforming Cu ions into CuNPs while EDA functions to aggregate the CuNPs into CuNWs. Such explanation was also suggested by other authors [11,12]. The role of hydrazine as an oxygen reductor and EDA as a capping or guiding agent can be used to understand the mechanism of other metal nano wire forming. In short, in the wet synthesis of metal nano wires, two agents play important roles in producing metal nanowires which are the reductor and the guiding agent. Both play important roles in forming the diameter and in the length of the wire. And such evidence also happens in the forming of AgNW [15]. Although we estimated that the ratio of length to diameter of the wires might be made higher, in the present experiment, we obtained the highest ratio to be 120 ± 30. It was smaller than that was obtained in Ref.[12] and [14], however, we believe that this number can still be increased using a correct ratio of hydrazine and EDA.

It should be noted that although the extracted solution of Cu NW was kept at -4 °C, the Cu NW still experienced oxidation as it was tested by X-ray diffraction as shown in the Fig. 5. The Cu_2O [111] plane appeared at 2θ = 35.8 while the rest of the peaks confirmed as Cu peaks using JCPDS 04-0836. Using this spectrum we found that the Cu NW powder was in the form of a polycrystalline fcc cube having 2θ peaks at 42.56, 49.76, 74.68 correlated to [111], [200], and [220] planes respectively. Further effort has still been done underway to increase the ratio of length to diameter as well as to stabilize it from oxidation.

CONCLUSION

In summary, we concluded that the variation the volume of EDA and hydrazine in the wet synthesis Cu nanowire can be used to obtain the different size of copper nanowire as well as nanoparticles. The result also indicated that there exists an optimal condition in term of volume ratio between hydrazine and EDA in which the targeted Cu nanowire can be accomplished using the synthesis. In this synthesis, we obtain the optimum condition of volumes of hydrazine and EDA are 0.15 mL and 1.5 mL, respectively, and the synthesis produces CuNWs with the length to diameter ratio to be 120 ± 30.

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